

Pipeline and Hazardous Materials Safety Administration Office of Hazardous Materials Safety

2023 Research, Development and Technology Forum

November 28, 2023



Pipeline and Hazardous Materials Safety Administration



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2023 Research, Development and Technology Forum

Yolanda Y. Braxton

November 28, 2023



Pipeline and Hazardous Materials Safety Administration

PHMSA Mission

To facilitate the safe transportation of energy products and other hazardous materials that are essential to our daily lives.



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OHMS Background

3.3 Billion Tons of Hazardous Materials Shipped Annually

1.2 Million Hazardous Materials Shipments per Day

Intermodal Partners with FAA, FRA, FMCSA, and USCG

International Role in the UN, IMO, and ICAO



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Operation Systems Division





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DOT Strategic Goals





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OHMS Research Focus Areas

Risk Management and Mitigation

Packaging Integrity

Emerging Technology

Technical Analysis to Aid Risk Assessment



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Strategic Goal Alignment



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OHMS RD&T- Research Programs

Small Business Innovation Research (SBIR) Program

Supports scientific excellence and technological innovation through the investment of Federal research funds in American small businesses

Directed by DOT's Volpe National Transportation Center



Interagency Agreements

Collaborating with our federal partners across the federal government

Research under these agreements foster relationships with other agencies and avoids redundant research efforts.



Broad Agency Announcement (BAA) Program

Competitive solicitation procedure used to obtain proposals for basic and applied research

Research solicited under a BAA attempts to increase knowledge in science and/or advance the state of the art

SAM, GOV®

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Lithium-ion Research Categorization and Analysis

Review the scope and results of Department of Transportation's lithiumion battery research projects documented in Department's repository and Open Science Access Portal (ROSAP)

Identify what research documentation exists in ROSA-P Understand the relevance, depth, scope, and results of documented research projects Identify where gaps in documented LiB research (housed in ROSA-P) exist



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RD&T Strategic Communication Plan

Building a strategic plan to increase our engagement with stakeholders to increase collaboration efforts.

Goal #1 Transparency

Increase transparency between program and stakeholders by providing information in a timely matter.

Goal #2 Research Partnership

Seek, strengthen and maintain collaboration efforts with existing and new research partners.

Goal #3 Utilization of Research

Increase stakeholder awareness and utilization of completed OHMS Research.



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RD&T Project Evaluation Framework

Develop a framework to be used to assess the effectiveness, value, and performance of RD&T projects throughout the project lifecycle.



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Questions?





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Research, Development and Technology

E-HazID – Integrated RFID, Sensing & Communication System for Safe Transportation of HAZMAT

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Need for Accurate ID & Monitoring of Hazmat in Transit



• Continuous monitoring of hazmat during transportation is crucial

• Inaccurate or damaged physical labels can hinder emergency response



https://www.hazmatuniversity.com/news/ blog-marking-and-labeling-hazmat-labels/







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E-HazID for Electronic HazCom & Safety Monitoring



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SBIR Phase I Research Objectives

Develop key E-HazID technologies & experimentally demonstrate their feasibility





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Phase I Accomplishments: E-HazID Tag



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- Miniaturized wireless tag, easy to install
- E-label & HazCom, easy to input & output
- Four microsensors to detect all major issues
- Integrated robust optical liquid leak sensor
- Battery lasts for one year



Phase I Accomplishments: E-HazID Software

- Firmware integrated into the tag circuit
- Mobile app serving as user interface
- Firmware integrated into the fixed radar circuit



Firmware Development



Mobile App Development

🛯 AT&T Wi-Fi 🔶

E-HazID

Shipping Info

Material

K Back

5:14 PM

Quantity: 55 gal

Package: Drum

Shipper: Newport Sensors, Inc.

Name: Isopropyl Alcohol

80%



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E-HazID tag successfully detected Isopropyl alcohol leakage within 30 seconds



See VOC Gas Leak Status



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E-HazID tag instantly detected liquid leakage (water)



See Liquid Leak Status



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E-HazID tag successfully detected a temperature rise of 2°C within 20 seconds



See Temperature Status



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E-HazID tag immediately detected overturning



See Orientation Status



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E-HazID Commercialization

Phase II Plan

- Develop an E-HazID system featuring dual wireless connectivity
- Conduct a month-long trial in collaboration with interested users
- Analyze collected data to train an AI algorithm for safety alerts based on sensor fusion



E-HazID Features and Benefits

- Standalone system equipped with micro wireless tags for rapid deployment
- Tag integrates electronic HazCom with various sensors for continuous monitoring and real-time detection/alerts of all safety issues
- Dual wireless modes ensure robust communication even w/o Internet
- Features a user-friendly mobile interface
- AI-driven system for reliable safety alerts and valuable business insights





• Flammable Gas • Flammable Solid



Oxidizer

Non-VOC Leak • Corrosive Material

Detectable Safety Issues

Organic Peroxide



Shock

• Anv



Temperature • Misc. Hazardous



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Contact Information

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Research, Development and Technology

23-PH4: Wearable PPE-Integrated Sensors for First Responders

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Triton Systems – Chelmsford, MA

- Since 1992, Triton transitions R&D concepts to manufactured products
- Private equity investments + public non-dilutive funds
- Market-based focus areas:
 - ✓ Personal Air Mobility
 - \checkmark Acoustics
 - ✓ Sensing Systems
 - ✓ Human Systems
 - ✓ Ocean Systems

- ✓ Robotics
- ✓ Specialty Materials
- ✓ Structures
- ✓ Sustainment
- ✓ Artificial Intelligence







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Triton Systems – Human Systems

- Human-centered design for delivering user-driven solutions
- Enhancing realism with prototypes and functional form models
- Methods include SME interviews and task-based prototype evaluations
- Through emphasis on the user, we improve design efficacy and increase user adoption





The Team



Cole Godzinski Principal Investigator, Mechanical Eng.



David Pierre, PhD

Product Lead, Bioengineering & Sensors



James Saunders Program Manager, Director



Doug Freitag Business Development, Director



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The Problem

- HAZMAT incidents occur in chaotic, task-saturated environments.
- Current technology:
 - Large, handheld, expensive, difficult to use with PPE, and can require difficult training and/or maintenance.



Image provided by consultant



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The Need

• PPE-integrated sensor

- Chemical detection for OSHA threshold limits
- High sensitivity, durability, multi-chemical detection
- Intuitive alerts
 - Visually and auditorily saturated environment \rightarrow Tactile display
 - Provide situational awareness and enhance communication



Image provided by consultant



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The End Users

- First Responders
 - Training Level: Operations (firefighters)
 » Defensive role: stay at a distance
 - Goal: Understand the context of the hazard to protect life, property, and the environment
- HazMat First Responders
 - Training Level: Technician/Specialist
 » Offensive role: respond, contain, stop the release
 - Goal: Identify and quantify the chemical hazard present



Higher Burden Image provided by consultant



Wearable Alerting Tactile Cues for Hazard Response



WATCHR's Components

- Sensor package with multi-chemical detection (outside)
- Washable tactile alerting display (inside)



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The Sensor

- Can be functionalized for multi-gas detection
- Up to 32 chips on a single sensor
- Detection redundancies reduce failure









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The Sensor – CO Detection



[•] Heme and Cobalt binding agents

- Baseline Sensor exposed to open air
 - $H 300 \text{ ppm CO} \rightarrow \text{immediate}$ detection
 - $I 0 \text{ ppm CO} \rightarrow \text{sensor recovery}$
 - $J 300 \text{ ppm CO} \rightarrow \text{immediate}$ detection
 - $K 0 \text{ ppm CO} \rightarrow \text{sensor recovery}$



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Sensor — Cobalt ---- Heme

Re

The Sensor – NH3 Detection



- Cobalt binding agents; 4 redundant Cobalt channels
- Baseline (b) Sensor exposed to nitrogen
- Increased linear exposure to NH3 from 10-100 ppm
- N NH3 reduced to 0 ppm
- No initial recovery



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The Tactile Alerting Display

- Printed circuits are configurable for different form factors
- Can withstand 100 plus washes
- Reduces cognitive burden
- Eliminates distraction and cuts through environmental noise





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The PPE Integration

- Sensor package integration includes:
 - Swappable sensor package
 - Integrated base stays on PPE
 - Pair to alerting display with NFC tag
 - Wireless communication between sensor, display, and response team





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Encapsulated Microbes for Bioremediation of Hazardous Material Spills

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Understanding the Problem and DOT Needs

•200,000 HAZMAT incidents

•More than a million barrels of hazardous liquids were spilled

•Two billion USD are spent

•Current cleanup methods are focused on immediate containment and physical removal

•Use of chemicals for remediation is neither environmentally friendly nor sustainable

•Short- or long-term bioremediation solution is therefore needed once the HAZMAT spill is contained or removed

•Bioremediation: Use of microorganisms to break down environmental pollutants



Status Quo Solutions and Limitations

•Microorganisms are widely used for bioremediation

- •Not storage stable and requires protection from the external environment
- •Loss of performance when exposed to UV
- •Microbes coated with synthetic or natural polymers

•Does not absorb hydrocarbons and swells in water

•Silica and Granular Activated Carbon (GAC) are emerging new substrates

•Excellent absorption capacity and environmentally safe. \underline{BUT}

•Not storage stable and requires protection from the external environment

•Loss of performance when exposed to UV



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Our Solution

•Encapsulated Microbes in Functionalized silica absorbent (CitraSil)

•Inherent stability to the microbes against temperature, pH, and UV

•Hierarchal particle morphology increases absorption capacity

•Anionic surface charges for increased microbial stability

•Handles land and waterfront spills

- •Low barrier to regulatory approval
- •Patent Pending Technology



Schematic illustration of the prototype (Phase I deliverable)





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Technical Data and Product Features



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Technical Data

Property	Value
Volatile matter (%)	Max 1.4
Density (g/mL)	0.3±0.05
Angle of repose (deg)	18-24
pH (1% aqueous solution)	4-6
Particle Size (microns)	450±25
Total Porosity (%)	77-87
Total Pore Area (m ² /g)	156
HAZMAT Sorption Capacity	240
(volume per 100 g of sample)	
Zeta Potential (mv)	-26

•Identified and produced absorbents to meet customer's specific needs



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Product Features



SEM of CitraSil (10% citric acid modified)



XRD of CitraSil (10% citric acid modified)



Zeta Potential measurements of CitraSil at various pH

- •High pore volumes for HAZMAT absorption
- •Engineered anionic surfaces enable high microbial storage stability
- •Can handle Hazmat spills in both land and waterways
- •Safe to handle and Environmentally friendly







Performance Evaluation



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Microbial Stability

- •Microbes are stable in the presence of a hydrocarbon mixture
- •Absorption and remediation in one step
- •Surface-modified absorbents meet the customer's stability requirements





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Bioremediation

- •Volatiles were analyzed using PTR-ToF
- •Lower concentration of hydrocarbons in microbial product
- •Significant Bioremediation within three days
- •Product is highly effective in bioremediating hydrocarbons



Microbial Remediation of Nonane: PTR-ToF Results



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Techno-economic Assessment TABA Support



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Commercialization Readiness Assessment Report

•TABA Recommendations

- •Differentiate from the top two competing products
- •Follow-up with potential partners
- •Immediate focus on off-shore marine spills and degrading xenobiotic compounds

•Techno-Economic Assessment

Revenue Projection (2029): \$9.85 million based on 4.9 million units soldCost per pound is \$3.9 to \$5.8



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TEAM

pd prioritydesigns









CrossMark

Bioremediation of hydrocarbon degradation in a petroleumcontaminated soil and microbial population and activity determination

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Human Centric Design and Prototyping

Hydrocarbon Degradation studies

Bacillus manufacturing and microbial stability testing



and Prototyping

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COMPACT BROADBAND LEAK DETECTOR FOR AUTONOMOUS VEHICLES

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Adelphi Technology Inc.



- Adelphi History
 - Started from SBIR program
 - Now leading maker of neutron generators
 - 18 Employees, \$4M annual revenue, majority engineers
 - Experienced with hardware product introduction

- New Opportunity with WKU
 - Gas analyzer technology started at Western Kentucky University
 - Broader market and attractive growth opportunity for Adelphi
 - Can combine novel technology with commercial experience
 - Spinning out new company



Conventional Gas Monitoring

- Conventional laboratory gas chromatographs (GCs) are not suitable for monitoring in the field.
- Conventional leak detectors: cross sensitive and cannot identify complex chemicals. Typically designed for simple gases.
- Adelphi compact GC advantage: monitoring of gases and volatile organic compounds (VOCs) in the field.





Adelphi Compact GC

- Broad dynamic range:
 broad range of detectable gases and broad range of concentrations
- Does not use PID/FID detector, utilizes solid state detector instead



- Modular design with interchangeable columns, detectors and software
- Completely portable for field use. Battery powered, no laptop attached



Adelphi Compact GC (continued)

- Automated detection and concentration measurements, operator is not involved
- Automated sample collection with the internal pump, no syringe injection needed
- Low cost. Many devices can be purchased for monitoring multiple points
- Multisensory chromatography with novel solid-state detector



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Adelphi Compact GC Architecture

A Carrier Gas Generation Pump **B** Sample Pump **C** Detector Module **D** GC Column Oven Assembly E Injector Module with Pre-concentrator and Cooling Fan F Microprocessor Control Board **G** Internal Battery **H** Sample inlet I Raspberry Pi 4 computer J 7" 720P LED touchscreen







Adelphi GC Operating Cycle



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Adelphi Novel Solid State GC Detector

- PPB level of detection
- Ultra-fast response and Recovery (ms)
- No long-term drift
- Great reproducibility (3% performance variations over all the products ever manufactured)





Dobrokhotov, V.; Larin, A. Doped, Metal Oxide-Based Chemical Sensors. U.S. Patent 10,132,769, Nov. 20, 2018.

Alexander Larin, Phillip C. Womble and Vladimir Dobrokhotov, Novel highlyintegrated MEMS based solid state detectors for analytical gas chromatography, Sensors and Actuators B (Chemical), Sensors and Actuators B 256 1057–1068 (2018). <u>https://doi.org/10.1016/j.snb.2017.10.046</u>

Vladimir Dobrokhotov and Alexander Larin, Multisensory Gas Chromatography for Field Analysis of Complex Gaseous Mixtures, ChemEngineering 3(1) 13-30 (2019). <u>https://doi.org/10.3390/chemengineering3010013</u>



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Integrated Detector Inside of a Flow-Cell





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CONVENTIONAL DETECTOR

Gas chromatogram of Mix. 3 by using conventional non selective MOX detector (a) zoomed image of light compounds and (b) the full gas chromatogram. (1. Carbon Monoxide 10 ppm, 2. Hydrogen sulfide 100 ppb, 3. Ethyl-Mercaptan 50 ppb, 4. Acetone 50 ppb, 5. Ethanol 50 ppb, 6. Benzene 10 ppb, 7. Unknown, 8. Toluene 10 ppb, 9. Water, 10. Ethylbenzene 10 ppb, 11. O-Xylene 10 ppb).

NOVEL DETECTOR

Gas chromatogram of Mix. 3: (a) zoomed image of light compounds and (b) the full gas chromatogram. (1. Carbon Monoxide 10 ppm, 2. Hydrogen sulfide 100 ppb, 3. Ethyl-Mercaptan 50 ppb, 4. Acetone 50 ppb, 5. Ethanol 50 ppb, 6. Benzene 10 ppb, 7. Unknown, 8. Toluene 10 ppb, 9. Water, 10. Ethylbenzene 10 ppb, 11. O-Xylene 10 ppb).





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- Efficient monitoring of hazardous leaks can only be achieved by using an integrated approach combining real-time sensors and compact gas chromatograph.
- Real-time sensor systems are ideal for sudden spikes in concentration.
- Real-time sensors are not as useful for long term trending as gas chromatography.
- Adelphi leak detection system utilizes both techniques. This approach adds another level of data verification and significantly enhances system redundancy.







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Real-Time Monitor Output





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Acetic Acid (3% Household Vinegar)





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Enamel Paint Thinner





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1% Methane in Synthetic Air




Integrating Real-Time Monitor with GC

Butane and Ethyl Mercaptan Mix





Modular Design: Column Specificity



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Modular Design: Quick Column Swap



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Modular Design: Wireless Communication



- An Xbee module mounted to a USB carrier board (a).
- An Xbee module is also attached to the GC controller board and mounted into the case. (**b**, **c**).
- High gain antennas have been attached to the pelican case as well as the receiver module (d).
- Data is exactly mirrored on both the USB and Xbee computers (e).



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Environmental Tolerance Testing under Vibration (a) and Fluctuating Temperature and Humidity (b, c).





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Transition to Industrial-Grade Design: Structural Optimization



- Currently, our instruments are being transitioned from computer-based systems to controller-based ones.
- The industrial grade secure Distech controller naturally replaced Raspberry Pi computer, which operates as the open-source ecosystem.
- Novel industrial grade control platform (Distech, ECY303-M3) for Adelphi leak detector was designed to provide universal control solution for device operation, web interface, automated calibration, data integration, process automation, and multi-point sampling.



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Transition to Industrial-Grade Design: Compact Stationary System





Web Interface: Web interface provides human to machine interface (HMI) through a web App or web browser. Currently, any mobile device with web browser can be used for control of the instrument.

Automated Calibration: The process of system calibration can be performed using a portable calibration system. The system consists of two channels (zero air and calibration gas of known concentration) connected to a gas mixing chamber.



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Transition to Industrial-Grade Design: Portable System



Process automation: The system is fully automated and samples chemicals, conducts measurements and reports the status without any involvement of an operator. Manual control from a remote location is also available as an optional feature.

Multi-point detection inside and outside the cargo area: The Distech controller supports communication with up to four remote modules ECx-Light which could be installed at distance of hundred meters from main controller. Each module enables monitoring from four independent locations. For the current design maximum amount for sampling units is equal to 16 (4x4).



Industrial-Grade System for Monitoring of Autonomous Vehicles



Industrial-grade system for monitoring of autonomous vehicles: compact GC used as communication hub for real-time sensors and equipped with the multichannel sampling system.



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Mobile Interface



1	1:13	. ∎∏ 50	G 💽	
0	Departme	nt of Transp	oortation	
-	APPLICATION_SETTINGS			
$\mathbf{\hat{o}}$	Application type	Natural Gas		
	Operating pressure	130	Hg	
~	Operating airflow	6	ml/min	
8	Column temperature	90	с	
	Column type	CarboWAX		
ă	Time of analysis	600	sec	
Ø	Purging time for pre-concentrator	15	sec	
	Sampling time	60	sec	
	Injection time	10	sec	
	Warm up time for GC	600	sec	
	Type of pre-concentrator	Carbo 153 TGX2343a TGX2343b TGX2343c		
	Pre-concentrator injection temperature			
	Sensor 1 type			
	Sensor 2 type			
	Sensor 3 type			
	Sensor 4 type	TGX2343d		
	Number of active sensors	3		
	Gasoline			
	Explosives			
A	Amonia 4			
1	✓ Natural Gas			

	11:12	al	t in the second s
2	<u>Departme</u>	nt of Transp	ortation
-	APPLICATION_SETTINGS		
\bigcirc	Application type	Natural Gas	
	Operating pressure	130	Hg
×	Operating airflow	6	ml/min
6	Column temperature	90	С
	Column type	CarboWAX	
õ	Time of analysis	600	sec
Ø	Purging time for pre-concentrator	15	sec
	Sampling time	60	sec
	Injection time	10	sec
	Warm up time for GC	600	sec
	Type of pre-concentrator	Carbo	
	Pre-concentrator injection temperature	153	
	Sensor 1 type	TGX2343a	
	Sensor 2 type	TGX2343b	
	Sensor 3 type	TGX2343c	
	Sensor 4 type	TGX2343d	
	Number of active sensors	3	
	Number of sampling channels	12	
	Passive sensor module enabled	TRUE	
	Multi-channel sampling system enabled	TRUE	
	Natural Cos	E	3



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Field Testing



Forbes

FedEx Teams Up With Elroy Air For Autonomous Cargo Drone Delivery



Adelphi is working with Elroy Air on the system implementation.

 Elroy Air is currently working with FedEx on autonomous cargo drone delivery.



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THANK YOU!



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Research, Development and Technology

LNG by Rail Quantitative Risk Assessment

and Worst Case Analysis

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LNG by Rail QRA and WCA Agenda

- •Introduction
- •Scope and Purpose
- •Quantitative Risk Assessment
- •Worst Case Analysis
- •Results
- •Discussion



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LNG by Rail QRA & WCA

- May 2022 PHMSA Contracted with ABSG Consulting Inc. (ABSG)
- Scope:
 - Perform Quantitative Risk Assessment and
 - Worst-Case Scenario Analysis of LNG Transport by Rail Car
- Prompted by TRB Report titled "Preparing for LNG by Rail Tank Car: A Review of U.S. DOT Safety Research, Testing, and Analysis Initiative."

National Academies of Sciences, Engineering, and Medicine. 2021. *Preparing for* LNG by Rail Tank Car: A Review of a U.S. DOT Safety Research, Testing, and Analysis Initiative. Washington, DC: The National Academies Press. https://doi.org/10.17226/26221.



Risk Model

Basic Risk Model = Frequency × Probability × Consequence



- Frequency is the likelihood of a given accident per train transit
- **Probability** is the likelihood of various event types resulting from various LNG releases
- **Consequence** is the estimated fatalities
- **Risk** is the estimated fatalities per train transit



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Quantitative Risk Assessment for LNG by Rail Project

Modeling Approach:

- Employed QRA best practices to estimate
 - (1) accident frequencies,
 - (2) conditional probabilities, &
 - (3) consequences based on Worst Case Analysis (WCA)
- Leveraged previous QRAs & authoritative references to support methodology
- Developed & implemented geospatial model using national rail network & high-definition population data for estimating impacts on populations

Train Types	Operations	Representative Routes
 Unit trains Manifest trains 	 Loading & unloading Transit Switching (manifest trains only) 	 Tioga, ND to Boston, MA Tioga, ND to Jordan Cove, OR Wyalusing, PA to Boston, MA Seminole, TX to Corpus Christi, TX



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Train characteristics

Unit Train Configuration

Туре	Count	Position(s) in Train
Locomotives (head end)	4	1-4
Buffer car	1	5
LNG tank cars	100	6-105

Manifest Train Configuration

Туре	Count	Position(s) in Train
Locomotives (head end)	4	1-4
Buffer cars & other railcars	5	5-9
LNG tank cars	20	10-29
Rail cars	76	30-105

Assumptions

- 105 car length
- 4 locomotives (212.5-ton weight each) for mainline operations
- 143-ton weight for LNG & all other types of rail cars
- 1st LNG tank car in manifest trains at position 10 (6th position from last locomotive)





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Representative Route Characteristics

Route		Origin	De	Length	
	City	Location	City	Location	(miles)
1	Tioga, ND	Alkane Midstream LLC Tioga ND	Boston, MA	Commercial Point LNG Plant	1,998
2	Tioga, ND	Alkane Midstream LLC Tioga ND	Jordan Cove, OR	Jordan Cove LNG Plant	1,460
3	Wyalusing, PA	Wyalusing PA	Boston, MA	Commercial Point LNG Plant	430
4	Seagraves. TX	Alkane Midstream LLC Seminole TX	Corpus Christi, TX	Corpus Christi Liquefaction Plant	721

		FR/	A Track C	ass			
Route	1	2	3	4	5	% of Route Signaled	% of Route with >20 MGT Traffic Density
1	2%	1%	7%	52%	38%	88%	85%
2	7%	2%	7%	22%	63%	86%	91%
3	6%	3%	45%	40%	6%	67%	9%
4	11%	2%	19%	65%	4%	68%	70%

- Route track characteristics inferred from FRA accident & crossings inventory data
- Speed of operations set to allowed track class limit with a maximum allowable speed of 50 mph



Wyalusing, PA to Boston, MA









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Risk Calculations by Operation



Accident Frequency & Release Size Probability Modeling

MODELING FACTORS

- Accident types
- Train characteristics
- Route characteristics
- Track types
- Speeds of operations
- Tank car characteristics
- Speed-dependent conditional probability of release estimates
- Loading/unloading factors



OPERATIONS & ACCIDENTS

Loading/ Unloading Accident Transit Derailment Transit Collision Switching Accident



Accident Frequencies

- Transit derailment based on track class, signalization, & traffic density: location specific rates
- Transit collision rate: 29 collisions/1B train miles
- Yard switching accident rates for manifest trains:
 6.43 derailments/1M cars processed
- Loading/unloading accident rate calculated based on: (1) piping, hose, valve, & pump failure, (2) operator connection error & (3) inadvertent movement of cars during transfer: 1 release/25K transfers

Traffic		FRA Track Class				
density (MGT)	Signaling	1	2	3	4	5
<20	Non-signaled	4.9E-06	1.9E-06	1.0E-06	5.9E-07	0.0E+00
	Signaled	7.4E-06	2.0E-06	8.1E-07	4.2E-07	7.3E-07
>=20	Non-signaled	8.4E-07	6.0E-07	2.2E-07	2.9E-07	0.0E+00
	Signaled	1.2E-06	6.6E-07	2.6E-07	1.4E-07	7.8E-08

Route	Route	Derailment Rate Per Trip & Train Mile	
1	Tioga, ND - Boston, MA	2.3E-07	
2	Tioga, ND – Jordan Cove, OR	3.8E-07	
3	Wyalusing, PA – Boston, MA	9.7E-07	
4	Seagraves, TX – Corpus Christi, TX	7.4E-07	



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Probabilities of Various Number of Cars Involved

POSITION-BASED DERAILMENT CONDITIONAL PROBABILITY

26-mph derailment example 0.14 Derailment Probability 0.10 0.10 0.10 0.00 Unit Position-based 0.06 0.04 0.02 0.00 30 40 50 60 70 80 0 10 20 90 100 Appapping 0.14 0.12 **Manifest** 0.10 Derailm 80.0 Position-based 0.06 0.04 0.02 0.00 20 30 0 10 40 50 60 70 80 90 100 Car Position in Train

- Considers the probability of derailment starting at a certain position
- Probability contributions of several rail cars being derailed from each of the positions to determine the position-based derailment probability





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Representative Release Sizes

- RA-19-01 : *Conditional Probability of Release (CPR) Estimates for Railroad Tank Cars in Accidents* provides probability of release size from a single tank car for both pressure and non-pressure cars for transit & switching
- Applied to choose 10 representative release size categories for transit & switching operations

Transit & Switching Release Sizes					
1.	½ car	6.	3 cars		
2.	1 car	7.	4 cars		
3.	1.5 cars	8.	5 cars		
4.	2 cars	9.	6 cars		
5.	2.5 cars	10.	7 cars		







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CPR determination

- CPR for LNG tank car design 113C120W9 is unknown
- Probability estimates for release sizes leverage RA-19-01 informed by:
 - Tank car design information, TRB study, FRA impact test
 - Operational characteristics: train speed & track type
- Method was not directly applicable to cryogenic tank cars, but estimates derived for two cases:
 - Coarse conservative: outer tank-only
 - **Coarse approximation:** tank with a combined thickness of the inner & outer tanks

TANK CHARACTERISTICS

- TC128B steel type
- 9/16-inch outer tank thickness
- 0.375-inch inner tank thickness
- Full head shield & jacket

	Speed (mph)			
CPR Case	25	40	50	
Coarse conservative	0.07	0.09	0.11	
Coarse Approximation	0.03	0.04	0.05	



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Risk Model

Basic Risk Model = Frequency × Probability × Consequence



- Frequency is the likelihood of a given accident per train transit
- **Probability** is the likelihood of various event types resulting from various LNG releases
- **Consequence** is the estimated fatalities
- **Risk** is the estimated fatalities per train transit



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Event Trees & Event Types

- Event trees used to describe the 5 event types
- Branch point probabilities defined the probability for each potential event type
- Probability estimates came primarily from other HazMat rail transport & hydrocarbon facility operating experience & failure data



4. BLEVE: Fireball

5. BLEVE: Overpressure

EVENT TYPES

Transit & Switching Event Tree



BRANCH POINT CONSIDERATIONS

• Immediate ignition

- Includes ignition by sources in area & by the train accident itself
- Using Hazard Class 2.1 rail accident data to inform this, plus comparison to published values

Delayed ignition

- Using suggested data from published studies
- Also considering insights from Hazard Class 2.1 rail accident data

• Transition to VCE

- Very likely outcome in more densely populated areas (e.g., houses, businesses, people)
- Congestion/confinement contributes to the transition
- Uses value consistent with published sources

• BLEVE from fire exposure

- Considers lessons learned from worst case analyses
- Uses value consistent with published sources; however, with limited data, a conservative value was selected.



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LNG by Rail WCA

Define accident scenarios that consider the most severe in the event of an accident involving the transportation of LNG via rail.

- •Task 3: Jet Fire Heat Flux on Adjacent Tank
- •Task 4: Valve or Line Damage Leak Consequences
- •Task 5: Cascading Tank Damage Due to Impinging Unignited LNG Pools
- •Task 6: Cascading Tank Damage Due to Heat Flux from Pool Fire
- Task 7: Rapid Phase Transition (RPT) Risk to First Responders
 Task 8: Vapor Cloud Explosion (VCE) Hazards from LNG Vapors in Congested/Confined Spaces
- •Task 9: BLEVE



LNG by Rail WCA Task 3 – Jet Fire Methodology

• Scenario: Overturned car in a fire relieving via PRDs which are directed toward another tanker (Jet Fire Impingement)





- Horizontal Jet Fire will release liquid LNG at its saturated temperature at the PRD setpoint pressure (75 psig PRD x 1.21 per API standards).
- Ignition is assumed given tanker is heated by an external fire that heats the outer-most cylindrical shell.
- Max 250 kW/m2; 10 ft wide section > 200 kW/m2, 23 ft wide section > 100 kW/m2



LNG by Rail WCA Task 4 – Valve/Line Leak Consequences Methodology

- •Modeling Assumptions:
- 3" valve leak
- Assume tank car pressure remains constant during release
- Pressure of 45 psig was used in previous TRB modeling The start to discharge pressure of the pressure relief value is 75 psig.



Leaks from damage to the valve box or lines result in flammable vapor clouds, fires, and explosions



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Task 7: Rapid Phase Transition Methodology

- Focus on RPT Risk to First Responders
- Three LNG compositions were analyzed; lean, design, and rich
 - Large puncture leaks (12" x 12") will empty a railcar in 55 sec and the pool will be vaporized after 2 min; therefore, RPT is not a risk for responders (occurs too fast)
 - Smaller leaks (3" valve) will create a RPT hazard for up to 20 min
 - Consequences from RPT are based on the TNT equivalent from work energy performed during the liquid to gas isentropic expansion

Distances are not significant; approaching an LNG pool this close would be a more significant fire risk should ignition occur

Alkane	Lean	Design	Rich
Methane	0.9797	0.9668	0.9318
Ethane	0.0137	0.0256	0.05
Propane	0.0012	0.0018	0.0089
n-Butane	0.0054	0.0058	0.0093



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Pipeline and Hazardous Materials Safety Administration [1] Aursand, E., Hammer, M., "Predicting triggering and consequence of delayed LNG RPT", Journal of Los Prevention in the Process Industries, Sept. 2018.

Task 8: VC Hazards - LNG Vapors in Cong. Areas Methodology

- Puncture of 7 railcars used in the WCA
- The multi energy method was used to predict overpressure and impulse
- Congestion assumptions for a rural and urban scenarios
 - The rural scenario will have 3% congestion with an average diameter of 6 in
 - The urban scenario will have 5% congestion with an average diameter of 4 in
- Spill pools were assumed to have an 8" thickness due to topography and drainage; maximum pool radius was 115 ft



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Task 9: BLEVE Methodology

- Occurs when a vessel heats up and fails with liquified gasses temperatures well above ambient bubble points
- 2 cases
 - Case 1: 100% full, 300 psig rupture (minimum burst pressure of tanker), assumes the PRDs are ineffective
 - Case 2 50% full; 75 psig PRD * 1.21 factor (API)
- Surface emissive power of the fireball assumed 508 kW/m2 (per TRB recommendation)
- CCPS equations used to calculate fireballs; FACET3D (ABS) used for blast effects
- BLEVE is considered a low probability event given the tanker design (double wall insulation) and recent testing experience



Fatality Summary

Task	Description	Hazard	Maximum Fatalities	
			Urban Day	Urban Night
3	3" valve leak	Flash fire	29	1
		VCE	27	187
		Jet fire	108	5
		Pool fire	223	20
8	7 puncture derailment	Flash fire	70	2
		VCE	1325	424
		Jet fire	*	*
		Pool fire	335	28
9	BLEVE	Overpressure	419	75
		Fireball	540	27

*Jet fires from a 12"x12" puncture are unlikely at the pressures considered; the large release rate will quickly reduce the tank pressure and the leak momentum will decrease to a spill which forms a pool




Conclusions

Task 3: Jet fire impingement on adjacent tankFailure not predicted but MLI will see high temperaturesTask 4 & 8: LNG leaks (3" valve and multiple punctures)

- Flammable clouds (flash fires)
 - The flammable clouds can be 100's of feet to over 1000 ft long and cover a significant area
 - Largest populations (daytime and urban) don't align with the largest cloud sizes (night time and rural)
 - Flash fire hazards produced the lowest maximum fatality estimates of all the hazard type considered







Conclusions (Tasks 4 & 8)

Vapor Cloud Explosions

- The 3" valve leak VCEs only produce significant fatalities in the Urban Night case
- The 7 puncture derailment VCEs are significant due to the large cloud sizes and they result in very strong explosions
- The VCE event has the highest fatality estimates; however, the probability that a derailment causing 7 punctures does not immediately ignite the release is low

Pool Fires

Likely overestimates fatalities for fires in urban environments as model does not consider exposure duration or potential escape indoors or shield behind buildings





Conclusions

- Task 7: Rapid phase transition
 - RPT of LNG can create small overpressure events equivalent to 5 to 12 lb of TNT
 - The lethality distance for these events was calculated to be around 15 ft (for 10%) lethality)
 - At this distance, 1st responders are at higher risk from fire should the spill ignite
- Task 9: BLEVE
 - Considered unlikely due to the double walled tank car design and prior tank car test
 - BLEVE takes a long duration fire exposure before the explosion allows for evacuation of the nearby populace
 - Should a BLEVE occur, consequences from overpressure can be severe
 - Fireball fatalities can be very high, but this is unlikely since people will move away from the burning tank car and/or find shelter inside a building.



Population overlay for fatality estimation



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Estimated Fatalities					
Maximum wind direction (NNE)					
Day	38.1				
Night	0.1				
Average of 16 wind directions					
Day	16.9				
Night	0.02				
Average of day/night fatalities					
Day/Night	8.5				

Population Distribution				
Day	93% Indoors			
Night	99% Indoors			

Indoor exposure zones 60.5% 37.1% 13.7% 2%

Outdoor exposure zones

Results presented in 7 dimensions

Operations

Transit

Switching

Loading/Unloading



Train Types

Manifest

Unit

- Tioga ND to Boston MA
 Tioga ND to Jordan Cove OR
- 3. Wyalusing PA to Boston MA
- 4. Seminole TX to Corpus Christi TX

Risk Categories

Very Low (< 1x10⁻⁸)
 Low (1x10⁻⁸ to 1x10⁻⁷)
 Medium (1x10⁻⁷ to 1x10⁻⁶)
 High (1x10⁻⁶ to 1x10⁻⁵)
 Very High (> 1x10⁻⁵)

Event Types

Pool Fire
Flash Fire
BLEVE Fireball
BLEVE Overpressure
Vapor Cloud Explosion

County Population Categories

<2500 people 2500 to 20K people 20K to 250K people 250K to 1M people

>1M people

Social Vulnerability Quartiles





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Risk per train by route, train type, & operation



Observations

- Per train, unit is 2.4x higher risk than manifest
- Per car, manifest is 2x higher risk than unit
- Switching ≈ transit risk for manifest trains averaged across routes
- Loading/unloading/ switching risk is highly dependent on location

risk

 Loading/unloading risk contributes 12% of manifest train risk & 25% of unit train



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Average risk per mile per train by route & train



Observations

- Route 3 has the highest risk rate due to higher population density in northeast U.S.
- Route 2 has the lowest risk rate due to sparse population in northwest U.S.
- The end of Route 1 is shared with Route 3 but the average is lower due to many more miles in low population areas

F-N curves by route & train type



Observations

- All routes and train types fall below the Unacceptable risk threshold
- Unit train risk is higher than manifest train risk
- Risks shown are on a per train basis, Risk Acceptance Criteria typically based on Annual estimates
- Note: Routes 1 & 3 have very similar FN curves after ~60 fatality threshold due to similar routing on final leg

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Risk per train (all routes) by operation, train type



Observations

- The BLEVE fireball event type is the dominant risk driver – it contributes 68% of risk across all routes and train types
- Pool fire is the dominant driver for loading & unloading operations



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Route risk for manifest train



Contact Information

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FULL-SCALE SHELL IMPACT IMPACT TEST OF A DOT-DOT-113C120W9 TANK CAR TANK CAR FILLED WITH WITH LIQUID NITROGEN

NAVE ACCEPTINI full-scale shell impact test (Test 13) of a DOT-113C120W9 tank car filled with liquid with liquid nitrogen (LN2). The test aimed to evaluate the puncture resistance of the resistance of the tank car design when subjected to an impact.



BACKGROUND (1/2)



BACKGROUND (2/2)

- HM-264 final rule published July 24, 2020
- Authorizes transportation of LNG in DOT-113C120W9 tank cars
- Additional operational controls

44994	Federal R	Register / Vo
DEPARTME	NT OF TRANSF	ORTATION
Pipeline and Safety Admi	Hazardous Ma nistration	aterials
49 CFR Part 180	s 172, 173, 174	, 179, and
[Docket No. P	HMSA-2018-002	25 (HM-264)]
RIN 2137-AF4	10	
Hazardous M Gas by Rail	Materials: Lique	efied Natural
AGENCY: Pipe Materials Sa (PHMSA), D (DOT).	eline and Hazar fety Administra epartment of Tr	rdous ation ransportation
ACTION: Fina	l rule.	
SUMMARY: Pf the Federal I (FRA), is am Materials Re for the bulk refrigerated	IMSA, in coord Railroad Admin ending the Haz gulations (HMF transport of ''M liquid,'' commo	lination with listration ardous {) to allow ethane, only known

DOT-113 FULL-SCALE IMPACT TESTING PROGRAM

Test #	Test Article	Lading	Impact Speed	Puncture
10	Legacy DOT- 113C120W	Water	16.7 mph	Yes
11	Surrogate DOT-113	Water	17.3 mph	No
12	Surrogate DOT-113	LN2	18.3 mph	No
13	New DOT- 113C120W9	LN2	22.1 mph	Yes



METHODS

- The shell of the outer tank is struck by a ~297,000-pound ram car equipped with a 12-inch by 12-inch impactor at its mid-height and longitudinally offset ~2.5 feet towards the A-end.
- Various instruments, including laser displacement transducers, pressure transducers, temperature sensors, and string potentiometers, are employed to measure critical parameters during the impact test.



CONCLUSION

The newly constructed DOT-113 tank car demonstrated double the peak force and absorbed energy compared to the legacy DOT-113C120W tank car, indicating improved puncture resistance.



FUTURE ACTIONS

- The research team will review the test data, photos, and videos to validate the pre-test finite element (FE) model.
- The model will be updated to reflect the actual impact conditions and used to investigate the puncture resistance of the DOT-113 tank car in real-world service scenarios.

CONTACT ME!

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Pipeline and Hazardous Materials Safety Administration Office of Hazardous Materials Safety

2023 Research, Development and Technology Forum

November 28, 2023



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Office of Planning and Analytics (OPA) Environmental Policy & Justice Division (EPJ) Carolyn Nelson, P.E., Director

Environmental Justice and Equity Considerations During the Transport of Hazardous Materials



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ANSPORTAT

To Protect People and the Environment From the Risks of Hazardous Materials Transportation



Terminology

Environmental Justice (EJ), Title VI, NEPA and other Non-Discrimination laws, and Equity are distinct elements, collectively they can contribute to the development of an equitable transportation system. These elements are regularly mistaken and used interchangeably, thus, making it essential to understand their differences.



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OPLOTINGUES SHEROUNE

WHAT IS NEPA?

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National Environmental = Edit MPolicy Act (NEPA) of 1969

- Second leve
 - Third level
 - Fourth level
 - Fifth leve



What is Environmental Justice (EJ)?

EO 12393 - Executive Order on Federal Actions to Address

Executive Order 12898, Federal Actions to Address Executive Order 12898, Federal Actions to Address Environmental Justice in Minority Populations and Low-Income Populations.

"...each Federal agency shall make achieving environmental justice part of its mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of its programs, policies, and activities on minority populations and lowincome populations..."

EO 12898, Section 1-101

On February 11, 1994, President William J. Clinton signed

-440,1

President Clinton signed E.O. 12898 on February 11, 1994



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What is Title VI?

Title VI of the Civil Rights Act of 1964

- Prohibits discrimination based on <u>race</u>, <u>color</u>, and <u>national origin</u> in programs and activities receiving Federal financial assistance.
- Provides that "No person in the United States shall, on the ground of race, color, or national origin, be excluded from participation in, be denied the benefits of, or be subjected to discrimination under any program or activity receiving Federal financial assistance."





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Addressing Discrimination under NEPA, EJ and Title VI

NEPA - Responsibility of Federal Agencies to not discriminate. As we conduct NEPA must evaluate our NEPA decisions to ensure actions do not lead to discrimination. As part of the NEPA process evaluate impacts of <u>all</u> actions of the project which includes impacts to EJ and Title VI communities.

EJ – When you have EJ communities, we must evaluate to what extent we have those impacts. (Disproportionately High and Adverse).

Title VI – Prohibits discrimination. Provides a mechanism to file a complaint if stakeholders/public feel federal actions are discriminatory.





NEPA, Environmental Justice & Title VI

WORKING TOGETHER



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Equity and Environmental

Justice

Biden Administration Executive Orders (EOs)

- EO 13985, "Advancing Racial Equity and Support for underserved Communities Through the Federal Government"
- EO 14008, "Tackling the Climate Crisis at Home and Abroad
- EO 14096, "Revitalizing Our Nation's Commitment to Environmental Justice for All"





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Environmental Justice - Equality vs Equity

Equality



The assumption is that everyone benefits from the same supports. This is equal treatment.



Everyone gets the supports they need (this is the concept of "affirmative action"), thus producing equity. Justice



All 3 can see the game without supports or accommodations because **the cause(s) of the inequity was addressed**. The systemic barrier has been removed.



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Whole of Government Approach to Addressing EJ & Equity

Environmental Justice (EO) 12898, "Federal Actions to Address Environmental Justice in Minority Populations and Low-Income Populations"

Executive Order (EO) 13985, "Advancing Racial Equity and Support for Underserved Communities Through the Federal Government" requires the Federal Government to "pursue a comprehensive approach to advancing equity for all, including people of color and others who have been historically underserved, marginalized, and adversely affected by persistent poverty and inequality."

Executive Order (EO) 14008, "Tackling the Climate Crisis at Home and Abroad," seeks to organize and deploy the full capacity of its agencies to combat the climate crisis. This includes a whole of government approach to advance environmental justice. It identifies covered programs and covered investments where "federal investments might be made toward a goal that 40 percent of the overall benefits flow to disadvantaged communities." {Justice40 Initiative }

Executive Order (EO) 14096, "Revitalizing Our Nation's Commitment to Environmental Justice for All", seeks to address environmental injustices thru federal governments.





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Pipeline and Hazardous Materials Safety Administration To Protect People and the Environment From the Risks of Hazardous Materials Transportation







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Pipeline and Hazardous Materials Safety Administration To Protect People and the Environment From the Risks of Hazardous Materials Transportation

EO 14096 - Executive Order to Revitalize Our Nation's Commitment to Environmental Justice

On April 21, 2023 President Joseph R. Biden, Jr. signed Executive Order 14096, Revitalizing Our Nation's Commitment to Environmental Justice for All

This EO outlines an ambition approach to Environmental Justice that is informed by scientific research, high quality data, meaningful federal engagement with communities, and by consultation with and respect for Tribal Sovereignties, self governments, and respecting cultural practices and indigenous knowledge.

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Executive Order 14096 - Confronting Environmental

*In*justice

The President's new executive order contains important new charges to agencies to demonstrate leadership and take action to:

- 1) Protect overburdened communities from pollution and environmental injustice through stronger action from federal agencies.
- 2) Confronts barriers to community participation in government decision-making.
- 3) Embed environmental justice for all into the DNA of federal agencies





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Environmental Justice Guidance and Equity

Public Involvement

- Developing a PHMSA-specific EJ Strategy
- Equity is the result of Environmental Justice
- Public involvement and a systematic interdisciplinary approach to outreach.
 - Agencywide *meaningful* public involvement





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RD&T for Environmental Policy and Health Impact Analysis

- Concepts:
 - Health effects of methane emissions
 - Transportation routing for transporting hazardous materials
 - Developing methodology specifically for identifying equity benefits
 - Look into possible cumulative health impacts and how they accumulate over time and events







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Research, Development and Technology

Equity Measure Research

November 28, 2023



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Objectives

- Contribute to Federal and DOT equity efforts:
 - Align with Executive Orders 13985 and 14091 and the DOT Equity Action Plan.
 - Align with DOT Strategic Goals: *Equity, Safety, Organizational Excellence*.
- Propose specific performance tracking metrics for different Office of HAZMAT Safety (OHMS) programs.





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Context

- Efficiency versus Equity.
 - Tradeoffs are necessary when setting equity targets and pursing equity goals.
 - The most efficient approach may not be the most equitable.
- Equity is <u>context specific.</u>
 - Different programs can and should measure and track equity differently.
 - Different types of data need to be collected depending on the program area.
- Program areas can apply practical approaches for equity measures.



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Methodology



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Project Approach





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Program Areas Studied

- Investigations and Inspections
- Outreach and Community Liaisons
- Special Permits
- Research, Development, and Technology
- Grants





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Defining Vulnerable Communities

Used the USDOT's Equitable Transportation Community (ETC) Explorer to assess the cumulative burden communities experience in five components:

- Transportation Insecurity
- Climate and Disaster Risk Burden
- Environmental Burden
- Health Vulnerability
- Social Vulnerability





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Social Vulnerability Components

Subcomponent	Metric				
Socioeconomic Status	Percent of population with Income below 200% of poverty level.				
	Percent of people age 25+ with less than a high school diploma.				
	Percent of people age 16+ unemployed.				
	Percent of total housing units that are renter-occupied.				
	Percent of occupied houses that spend 30% or more of their income on				
	housing with less than 75k income.				
	Percent of population uninsured.				
	Percent of households with no internet subscription.				
	Gini Index.				
Household Characteristics	Percent of population 65 years or older.				
	Percent of population 17 years or younger.				
	Percent of population with a disability.				
	Percent of population (age 5+) with limited English proficiency.				
	Percent of total housing units that are not mobile homes.				



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Defining Vulnerable Communities

- The social vulnerability metrics were compiled and converted to scores for US Census Tracts.
- Following ETC methodology, the top 35% of Census Tracts were considered vulnerable.



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Results



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Investigations and Inspections



Proposed Measure:

 Percentage of shipper inspections occurring in socially vulnerable areas (compared to the location of all known shippers) <u>nationally</u> and regionally.



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Outreach and Community Liaisons (CL)

Proposed Measures:

- Systematically measuring percentage of outreach events serving socially vulnerable areas nationally and <u>regionally</u>.
- Track progress towards Spanishlanguage translation goals of outreach material.





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Outreach and Community Liaisons (CL)

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- Systematically measuring percentage of outreach events serving socially vulnerable areas nationally and <u>regionally</u>.
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REQUISITOS DE TRANSPORTE DE MATERIALES PELIGROSOS

Guía impresa de Capacitación, empaque y embarque para transporte de materiales peligrosos.

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WWW.PHMSA.DOT.GOV



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Special Permits



Proposed Measure:

- Percentage of applicants and accepted special permits by equity consideration (i.e., small business, minority-owned, woman-owned, etc.).
- Track equity impacts of special permit conversions.



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Research, Development, and Technology

Proposed Measures:

- Percentage of research funds that go to small businesses, womenowned businesses, and minorityowned businesses.
- Track equity impacts of specific research efforts and programs.





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Grants



Proposed Measures:

- Percentage of funds awarded by grantee and subgrantee type (i.e., state, local, tribal).
- Potential for location-based (urban vs. rural) analysis if more data are collected.



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Serious Incident Analysis



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Serious Incident Analysis

• OHMS's defines an incident as *serious* if the incident resulted in one or more of the following items:

Serious Incident Definition

a fatality or major injury caused by the release of a hazardous material

the evacuation of 25 or more employees or responders or any number of the general public as a result of release of a hazardous material or exposure to fire

a release or exposure to fire which results in the closure of a major transportation artery

the alteration of an aircraft flight plan or operation

the release of radioactive materials from Type B packaging

the suspected release of a Risk Group 3 or 4 infectious substance

the release of over 11.9 gallons or 88.2 pounds of a severe marine pollutant

the release of a bulk quantity (over 119 gallons or 882 pounds) of a hazardous material.





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Serious Incident Analysis





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Key Takeaways

- Equity is context specific.
- OHMS is well positioned to incorporate practical equity measures into their diverse program areas.
 - Existing data can be used to retrospectively track performance from an equity perspective and prospectively inform program area decisions.
 - New data can be collected and incorporated.
- Future work will explore program areas further with case studies and will integrate proposed measures into OHMS performance tracking.



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Discussion and Contact Information

- What other factors should be considered?
- Who should we engage with on this topic?

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Pipeline and Hazardous Materials Safety Administration



Pipeline and Hazardous Materials Safety Administration Office of Hazardous Materials Safety



Research, Development and Technology Deactivation of Damaged, Defective, and Recalled (DDR) Batteries Gordon Waller, Rachel Carter, Corey Love | U.S. Naval Research Laboratory

November 28, 2023



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Batteries contain energy even at the end of life!

- Electrochemical energy (state-of-charge > 0%).
- Stranded energy (inaccessible Li deposits in a lithium-ion battery, cells/batteries with safety fuses activated).
- Chemical energy (flammable electrolytes, reactive compounds).

Project Goal: Develop a simple, cost effective, and broadly applicable methods to de-energize end of life batteries.







"Safety of Lithium-ion Cells and Batteries with Varying States-of-Charge". Joshi, T, et al. 14, 2020, Journal of the Electrochemical Society, Vol. 167.

- Researchers at Underwriters Laboratories (UL) reported on effect of SOC on LIB failure during external heating
- Some cell types (Cell A; NCA 18650 and Cell C; NCM 26650) showed thermal runaway at 15% SOC, but none at 0% SOC
- SOC has a strong influence on maximum temperature during thermal runaway and a weaker influence on onset temperature of thermal runaway for all chemistries

Deactivation Target: 0 V



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Method	Flexibility	Deployability	Affordability	Safety	Limitations
Saltwater Immersion	High	High	High	Moderate	Corrosion, generation of H_2
Electrical Discharge	Moderate	Moderate	Low to Moderate	High	Many require dynamic load bank / manual interaction with energized terminals
Shredding	Moderate	Low	Low	Low To Moderate	Requires preceding deactivation step or inert / cryogenic conditions

Literature survey of existing deactivation methods suggested saltwater immersion was a reasonable "one size fits all" option, with corrosion being a major barrier to efficacy.

"Deactivation of End-of-Life Batteries", G.H. Waller, R. Carter, C.T. Love, NRL/6170/MR— 2023/3 (2023), Accessible on DTIC



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 \geq 50% SOC and undergo thermal runaway with external heating.





Only cell in 5.8 wt% NH_3HCO_3 undergoes thermal runaway with external heating. Cells in 3.5 wt% NaCl and 11 wt% $NH_4H_2PO_4$ have OCV <0% SOC.







Positive tab connected to cell header in electrically



Top of jellyroll in NaCl discharged and electrically discharged cells shows only NaCl discharged cell. cells have been breached.

NaCl discharged electrodes

Electrically discharged electrodes



NaCl discharged header







- Electrical discharge (external short circuit) avoids hydrogen generation and corrosion, however existing methods are not ideal.
- Can we improve on the limitations of the external short circuit method?











Concept Electrically conductive water-based gel

- Water soluble polymer is used to encapsulate conductive carbon. Gel flows onto / into battery cavities to create an electrical discharge pathway. Conductivity increases as water evaporates.
- Polymer utilized is non-toxic and low cost no recovery of gel is required.













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Gel applied across header with shrink wrap removed.





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18650 LIB Cells discharged to 0V by electrically conductive gel show no signs of thermal runaway when heated to 180 °C.





18650 LIB Cells discharge to 0V by electrically conductive gel show have significantly lower concentrations of every measured gas species.



• Deactivation using electrically conductive gel was demonstrated on multiple cell formats / chemistry and results in a complete elimination of thermal runaway behavior and a significant decrease in gas concentrations with external heating

• Future work is focused on improving gel application method and demonstrations using more relevant battery packs.



Contact Information

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Research, Development and Technology

Sodium-ion Battery Testing



Rachel Carter, Gordon Waller, Corey Love | U.S. Naval Research Laboratory

November 28, 2023



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Problem Statement:

Sodium-ion Batteries are quickly entering the global market. Companies suggest higher safety. **Overall Goal:**

Preliminary safety and performance validation for safe transport



Batteries 2019, 5(1), 10

- Capable of 0 V Storage
- Fast Charging
- Aqueous and non-aqueous electrolytes
- Wide range of anode and cathode materials



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Company (Origin)	Nominal Voltage (V)	Nominal Energy Density (Wh/kg)	Cathode Material	Unit Cell Size (g); Form factor	Other Notes
	3.6	262	NCA; LiNi _x Co _y Al _z O ₂	46 18650	High energy
	3.3	113	LFP LiFePO4	76 26650	High safety; high power
	1.8	22	Prussian Blue Na2Fe[Fe(CN)6]	305 Pouch	High safety/low energy; aqueous;
	1.8	25	Prussian Blue Na2Fe[Fe(CN)6]	800 pouch	New pouch with 130 A nomina charge current
Covered	3.6	80	NVP Phosphate Na ₃ VO _x (PO ₄) ₂ F _y	33 18650	High safety; high power;
or Distro	3.1	140	Layered metal oxide NaNi _{1-x-y-z} $M^1 \overset{2}{\underset{x}{}} \overset{3}{\underset{x}{}} M_y M_z O^2$	660 Pouch	competitive with LFP; planned in FY23
Α	3.0	128	Na(NixFeyMnz)02	40 18650	Arriving any day
	3.2	160	Prussian White (R-Na1.92Fe[Fe(CN)6])	Prismatic and Large Cylindrical	FAR Regulated
	3.2	145	Prussian White	Pouch, 26650, 32138	FAR Regulated
	3.2	~100	Prussian White (R-Na1.92Fe[Fe(CN)6])	cylindrical	Recently began selling product
	2.6	~100	High temperature chemistry (SS) NiCl ₂	Pouch	No product yet; Solid state









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Will be tested in 24

Tested in 22-23



Failure-Mode Testing



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Company Name	Cathode Type	Spec ED Confirmation- color indicates agreeance	Accelerating Rate Calorimetry – color indicates severity	Gas Analysis- color indicates toxicity	Nail Penetration- color indicates severity			
Covered for Distro A	NCA; LiNi _x Co _y Al _z O ₂	Complete FY23	Complete FY23	Complete FY23	Complete FY23	On time		
	LFP LiFePO ₄	Cells in hand	Cells in hand					
	Prussian Blue Na2Fe[Fe(CN)6]	Complete FY22	Complete FY22	Waiting on replacement parts	Waiting on replacement parts	Safer		
	Prussian Blue Na2Fe[Fe(CN)6]	Cells procured						
	NVP Phosphate Na ₃ VO _x (PO ₄) ₂ F_y	Complete FY 22	Complete FY22	Complete FY23	Complete FY23	Dangerous		
	$NaNi_{1-x-y-z}$	Cells quoted but not ready to ship						
	Na(NixFeyMnz)O2	nz)O2 Cells shipped						



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Cell Type	LIB (NMC)	LIB (LFP)	SIB (VPF)	SIB (FeCN)	
Capacity					
(Ah)	3	1.1	0.7	4.5	
Specific heat, c _p					
(J/gK)	0.9	0.95	1.05	2	
Mass					
(g)	45	39	33	305	
Onset temp					
(°C)	125	140	55	170	
Max T rise					
(°C/min)	5000	100	0.1	0.18	
Temp at Max					
Rise (°C)	400	220	120	300	
Max Heat flux					
(W)	3375	62	0.06	0.94	
Enthalpy					
(kJ)	20	7	7.8	100	
Heat of					
reaction (J/g)	600	200	235	250	
	Batteries 2017, 3	Batteries 2017, 3			
Data Source	(2), 14	(2), 14	this work	this work	
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Gas Analysis Testing



Cell Type	SOC	Capacity (Ah)	Voltage (VDC)	Mass (g)	Wh/k g
Li-ion 18650	22%	0.75	3.59	45.8	59
Na-ion 18560	100%	0.7	4.25	33	77

- Li-ion 18650 at shipping SOC and Na-ion 18650 at 100% SOC were heated at 1-2 °C per minute inside of a pressure vessel.
- Vessel was purged with nitrogen for 30 minutes prior to heating and purged continuously during testing.
- All exhausted gases (N₂ + gases produced by battery failure) were flowed through an FTIR gas cell.





- Pressure Vessel (PV) contains all gas produced during LIB testing. Limited to small cells but contains all evolved gas.
- Fluoropolymer heated sample line at 180 °C minimizes condensation of evolved gases and reactions with acid gases (e.g. HF).
- FTIR uses 2M gas cell to measure many species of interest in the ppm to % range





Voltage drop occurs at 102 minutes / 129 °C before onset of selfheating. Self heating exceeds 5 °C/min at 179 °C and 3 of 4 cells reach a maximum temperature of ~700 °C, Test 4 material ejected

Voltage drop occurs at 64 minutes / 100 °C when self-heating exceeds 5 °C/min. Cell temp reaches a maximum of ~136 °C due to self-heating at 70 minutes, then continues to heat with chamber.

150

Test Time (minutes)

Na-ion 100% SOC

voltage (VDC)

Cell

(bar),

en

Press

Vessel

300

Cell Temp (Test 1)

Cell Temp (Test 2)

250

Pressure

- Voltage

200

200

175

50

25

50

100



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	Li-ion (18650	Na-ion 18650		
Species	Avg. max (ppm)	Calc. vol (mL)	Avg. max (ppm)	Calc. vol (mL)	
Carbon Dioxide	1.1E+05	474	1.2E+03	47	
Carbon Monoxide	4.2E+04	132	3.5E+02	8.3	
Hydrogen Cyanide	1.2E+02	-	-	-	
Hydrogen Fluoride	6.2E+02	10	1.4E+01	1.1	
Hydrogen Chloride	2.5E+01	-	-	-	
Methane	9.6E+03	34	4.5E+02	3.1	
Ethene	1.9E+03	-	1.0E+03	-	
Propene	1.9E+03	-	1.2E+03	-	
Propylene Carbonate	1.6E+02	-	1.6E+02	-	
Diethyl Carbonate	2.5E+02	-	3.2E+02	-	
Dimethyl Carbonate	7.4E+02	-	9.2E+02	-	

- Gases associated with electrolyte decomposition are much lower for Na-ion than Li-ion at equivalent energy density, while solvent vapors are comparable.
- Volumes of gases calculated by using ideal gas law assumptions and flow rate through FTIR exhaust (assumed to be constant but we know it's not). All values are ~10x lower for Na-ion than Li-ion.



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Li-ion 22% SOC



Na-ion 100% SOC





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- Early commercial Na-ion batteries evaluated
 - Promising rate capability
 - Capable of 0V storage
 - Thermal Runaway Risk found to be much lower than Li-ion but energy density is low
- Nail penetration
 - Similar heat rates from each cell
 - Different types of gases detected
- Gas Analysis
 - At least an order of magnitude lower gas production from the 18650 Na-ion compared to low SOC 18650 Li-ion

Next Steps

- Acquire higher energy density Na-ion cells and compare to LFP cells
- Nail penetration of Natron



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DOT PHMSA Mr. Joshua Davis- lead Dr. Erica Wiener Mr. Andrew Leyder



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LI-ION **I** LOCKER

Research, Development and Technology

ESSPI.

BLISS (Battery Logistics Integrated Safety System)

November 28, 2023



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BLISS - The Project



- USDOT/PHMSA funded research
- Government/industry partnerships
- Multi-year/multi-phase project
- Specialized battery transport, storage, and charging systems



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The Problems



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The Problems

New EV batteries burn in a truck on a highway outside of Detroit (2019). (Photo credit: WJRradio.com) Felicity Ace burns in the Atlantic Ocean (2022). (Photo credit: Netralnews.com)





Battery warehouse burns in Morris, Illinois (2021). (Photo credit: theloadstar.com)





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The Problems



- Firefighter entry with limited PPE
- Large explosions in sequence. The move to a defensive posture took too long
- Firefighters told by the owner that they shouldn't use water because there were, "lithium-ion batteries inside"
- How did fire spread?



- Truck explosion/deflagration at Birmingham truck stop
- Massive multi-directional pressure pulse
- Disassembled the trailer box
- Broke the spine of the trailer rated at 50,000 lbs.
- Limited fire spread



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BLISS – The Solutions

The Solutions



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BLISS – The Solutions – X Carry Container

Safe Battery Transport, Storage, and Charging Systems



DNOC System Detection/Notification/Operations/Communications

- Mitigation/Containment
- Monitoring/Detection
- Fire Suppression (large-format)
- Pressure Venting
- Toxic Gas Control
- Audible/Visual Notification
- Global Failure Communications



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BLISS – The Solutions – Battery Logistics Trailer

Safe Battery Transport, Storage, and Charging Systems



- Full DNOC system
- Includes active fire suppression, pressure and toxic gas control, and ventilation (EVACS)
- TRL 4
- Ready for extended design and development
- Appropriate for post failure event cleanup





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BLISS – The Solutions – Battery Logistics Trailer

Safe Battery Transport, Storage, and Charging Systems



- Prototype displays ability to transport battery packs, containers and 50-gallon drums
- Finished version can be specific to a specific type of container



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BLISS – The Solutions – ISO/Conex

Safe Battery Transport, Storage, and Charging Systems



- EV battery pack, module and cell transport and storage
- Closed-loop system can be used for transport and permanent/semipermanent storage
- Plug-in fire suppression and ventilation capability



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BLISS – The Solutions – ISO/Conex

Safe Battery Transport, Storage, and Charging Systems



- E-mobility charging KIOSK
- Designed based on work with NYC and FDNY
- Full DNOC system
- TRL 6
- Provides solution for indoor/outdoor SAFE charging
- Great opportunity for USDOT/PHMSA



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BLISS – The Solutions – "Smart Fire Blanket"

Safe Battery Transport, Storage, and Charging Systems



- EV/battery "Smart Fire Blanket"
- Monitors, detects, notifies, and communicates failure
- Blanket function controls fire and off-gassing
- Full DNOC
- TRL 7
- Q1 2024 pilot with 25 companies including GM, Honda, Stellantis, etc.





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BLISS – The Solutions – "Smart Drum"

Safe Battery Transport, Storage, and Charging Systems



- EV/battery "Smart Drum"
- Monitors, detects, notifies, and communicates failure
- Specialized CAP and lid unit
- Full DNOC
- TRL 7
- Q1 2024 pilot with 15 companies including GM, Honda, Stellantis, etc.



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BLISS – The Solutions – "Smart Fire Blanket"



BLISS Burn Testing Detroit Fire Department





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BLISS – Thank You

Safe Battery Transport, Storage, and Charging Systems



Thank You

contact: ron@esspi.com



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Research, Development and Technology

In-Field Magnetometry for Determination of LiB SOC and SOH

Dr. Joshua R. Biller

November 28, 2023



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Housekeeping

Information relayed in this presentation is covered by:

- SBIR Data Rights under DOT 6913G623P800063
- Patents pending with USPTO
 - Provisional #63/338,710 "Non-Contact Method for Non-Destructive Evaluation of Lithium Ion Batteries with Optically Pumped Magnetometer", filed 05/05/2022
 - Non-provisional #18/144,122 "Non-Destructive Evaluation of Lithium Ion Batteries", filed 05/05/2023



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About TDA Research Inc.





Golden Facility -2

• In Business for 36 years

- Privately held—8 partners, all active in daily operations
- ~130 employees, 33 Ph.D.'s chemistry/engineering
- Over \$28 million in annual revenue

• Facilities

- Combined 75,000 ft² laboratory and office space near Denver, Colorado
 - Synthetic Chemistry
 - Materials Testing
 - Defense & Aerospace
 - Sensor Technologies







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Lithium-Ion Batteries (LiB)



https://evolt.aevt.org/news/view/11

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Problem or Opportunity



He, X.; Hu, Z.; Restuccia, F.; Fang, J.; Rein, G., Applied Thermal Engineering 2022, 212, 118621.

No currently available non-contact and non-destructive evaluation (NDE) techniques for SOC or health monitoring of LiBs

- Shipment: Evaluate SOC or health prior to or during shipment
- First-Responders: Evaluate the likelihood of thermal runaway occurring at crash site





A LiB as an Inadvertent Magnet

Q: What are the overlapping characteristics of a bar magnet and a 18650 LiB?



A: Arrangement of microstructural ferromagnetic units determine a macro-scale magnetism



Air Force Study - 18650 LFP



accelerated lifetime.

AF FA8649-20-P-0968



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Air Force Study - 18650 LFP



In one case (LFP), a larger starting magnetic field signature correlated with longer cycling until 80% capacity fade was reached



DOT Work - NCA 18650



Visualizing the 3D, anisotropic magnetic field of a NCA 18650 battery

6913G623P800063



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Magnetic Map of 100 - 18650 LFP

LFP Cells: Z-Axis Vector





The magnetic field (Z-direction) of 100 LFP 1850 collected in ~30 minutes



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Magnetic Map of 100 - 18650 NCA

NCA Cells: Z-Axis Vector



The magnetic field (Z-direction) of 100 NCA 1850 collected in ~30 minutes

6913G623P800063



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E-Bike Battery



Shockproof Shell Structure Built-in Top A Grade Cells



The magnetic field (Z-direction) of 100 a commercial E-bike battery shows this information can still be collected in 18650 "packs"



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Lab to In-Field





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Summary

• LiB as an "inadvertent" magnet

- Cathode chemistries LCO, LFP, NCA
- 18650 geometries
- Singles, multiple open potential, multiple in series for larger battery pack
- Calibrating magnetic field signature with electrochemical characteristics
 - SOC NCA, LFP
 - SOH LFP
- Current Efforts
 - Magnetic field change in full battery pack while energized
 - Interpretation of "bulk magnetic field" of a collection of 18650 to enhance throughput for SOC & SOH screening





Contact Information





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Mr. Joshua Davis, PM Mr. Jorg Kaltenegger Dr. Michael Klem



David Long, EE, ME

Circuit board design and construction Precision machining Support with data collection and software design





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2023 Research, Development and Technology Forum

Andy Leyder

November 28, 2023



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OHMS RD&T Future Research Initiatives & Program Priorities



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Exploring Potential Rail Research Projects

Potential Research Area #1

Evaluate Tank Car Safety Materials & Coatings



Potential Research Area # 2

Performing Risk Assessments & Identifying Prevention & Mitigation Strategies **Potential Research Area #3**

Performance Validation on Tank Car Instruments





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Climate Change and Sustainability Research

Researching Recycled Plastics used for hazardous material packaging



Assessing the risk & mitigation methods with transporting Hydrogen and Co2



Pinpointing innovative and emerging technology to address climate change.



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Lithium-ion Batteries & Next Generation Batteries

Continue assessing evolving challenges with transporting lithium-ion batteries.

Identifying and Researching emerging battery chemistries and technologies. Detecting novel and emerging methods to transport lithium-ion batteries.







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Emerging Technology

Engaging with Federal Partners on Autonomous Vehicle Research Seeking cutting edge technology and materials for packaging



Researching the use of Predictive Analytics and Sensing Technologies.





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Program Priorities

RD&T Research Program

Small Business Innovation Research (SBIR) Program

- Continue working with our existing Small Business.
- Prepare for FY 24 SBIR solicitation.
- Continue to seek out SBIR topics



Federal Partners

- Continue to collaborate with existing partnership with our federal partners.
- Foster new collaboration efforts with other federal partners.



Subject Matter Expert Research

- Engage with internal and external SMEs on research topics.
- Identify potential new research projects driven by SMEs.





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Program Priorities



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Questions?





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